



EDGEWOOD

CHEMICAL BIOLOGICAL CENTER

U.S. ARMY SOLDIER AND BIOLOGICAL CHEMICAL COMMAND

ECBC-TR-091

**EXPERIMENTAL PROCEDURES FOR THE MEASUREMENT
OF POLYMER SOLUBILITY AND RHEOLOGICAL PROPERTIES**

**Wendel J. Shuely
Brian S. Ince**

RESEARCH AND TECHNOLOGY DIRECTORATE

November 2001

Approved for public release;
distribution is unlimited.



Aberdeen Proving Ground, MD 21010-5424

20020207 045

Disclaimer

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorizing documents.

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave Blank)		2. REPORT DATE 2001 November		3. REPORT TYPE AND DATES COVERED Final; 97 Oct - 99 May
4. TITLE AND SUBTITLE Experimental Procedures for the Measurement of Polymer Solubility and Rheological Properties			5. FUNDING NUMBERS PR-622384/ACB2	
6. AUTHOR(S) Shuely, Wendel J., and Ince, Brian S.				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) DIR, ECBC, * ATTN: AMSSB-RRT-PC, APG, MD 21010-5424			8. PERFORMING ORGANIZATION REPORT NUMBER ECBC-TR-091	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES *When this work was started the U.S. Army Edgewood Chemical Biological Center (ECBC) was known as the U.S. Army Edgewood Research, Development and Engineering Center (ERDEC).				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) The rheological evaluation of viscoelastic polymer solutions is important in characterizing two-phase flow, aerodynamic breakup, dynamic contact angle and spreading behavior, and adhesive transfer of solutions between surfaces. The preparation and property measurement of polymer solutions is an important aspect of several of these investigations and rather than report these methods separately, the development of these techniques is documented in this methodology report. The experimental procedures and calibration techniques developed for rheological research provided reliable, standardized methodology for investigation of the viscoelastic behavior of polymer solutions.				
14. SUBJECT TERMS Rheology Rheometer Viscoelasticity			15. NUMBER OF PAGES 27	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED		18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED		19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED
				20. LIMITATION OF ABSTRACT UL

Blank

PREFACE

The work described in this report was authorized under Project No. 622384ACB2, Non-Medical CB Defense. This work was started in October 1997 and completed in May 1999.

The use of either trade or manufacturers' names in this report does not constitute an official endorsement of any commercial products. This report may not be cited for purposes of advertisement.

This report has been approved for public release. Registered users should request additional copies from the Defense Technical Information Center; unregistered users should direct such requests to the National Technical Information Service.

Acknowledgments

The authors acknowledge William Bunting, Vince McHugh, and Seok Hong for the feedback and advice they provided during these studies. The authors also thank Donna Smith, Carolyn Sullivan, and Patsy D'Eramo, Technical Library, for their assistance in obtaining literature.

Blank

CONTENTS

1.	INTRODUCTION	7
2.	POLYMER SOLUTION PREPARATION AND SOLUBILITY DETERMINATION	8
2.1	Equipment and Procedures	8
2.2	Solubility Observations	9
3.	DILUTE SOLUTION MEASUREMENTS OF LIMITING VISCOSITY NUMBER	9
4.	RHEOLOGICAL MEASUREMENT PROCEDURES	10
4.1	Instrumentation	10
4.2	Instrumental Conditions	11
4.3	Rheometer Procedures	11
5.	RHEOMETER CALIBRATION	13
5.1	Calibration of Torque and Normal Forces	13
5.2	Torque Force Calibration, 10 g-cm Full Scale	13
5.3	Torque Force Calibration, 100 g-cm Full Scale	14
5.4	Normal Force Calibration, 10 g-cm Full Scale	15
5.5	Normal Force Calibration, 100 g-cm Full Scale	16
6.	RHEOLOGICAL STANDARD FLUIDS	17
7.	CONCLUSION	20
	LITERATURE CITED	25
	APPENDIX - INSTRUMENTATION AND EQUIPMENT EMPLOYED FOR POLYMER SOLUTION PREPARATION	27

FIGURE

Rheological Plot of First Normal Stress Difference (FNSD) Versus Shear Rate for NIST Standard Reference Material 1490 at 24.9 to 25.1 °C (see Table 7, Experiment 165f)	24
--	----

TABLES

1. Rheometer Experimental Condition for Measuring Viscoelastic Properties of Semi-Dilute Polymer Solutions	12
2. Newtonian Viscometric Calibration Fluid Examples	18
3. Rheological Reference Material Examples for Apparent Viscosity and First Normal Stress Difference (FNSD)	18
4. Apparent Viscosity and First Normal Stress Difference (FNSD) Calibration Values as a Function of Shear Rate at 25 °C for National Institute of Standard Technology (NIST) Rheological Materials	20
5. Rheological Measurements of Shear Rate Versus First Normal Stress Difference (FNSD) for Standard Reference Material Viscoelastic Nonlinear Flow Behavior	21
6. Rheological Measurements of Shear Rate Versus First Normal Stress Difference (FNSD) for Standard Reference Material 1490 Lot 810608 as a Performance Calibration for Viscoelastic Nonlinear Flow Behavior	22
7. Rheological Measurements of Shear Rate Versus First Normal Stress Difference (FNSD) for Standard Reference Material 1490 Lot 580905 as a Performance Calibration for Viscoelastic Nonlinear Flow Behavior	23

EXPERIMENTAL PROCEDURES FOR THE MEASUREMENT OF POLYMER SOLUBILITY AND RHEOLOGICAL PROPERTIES

1. INTRODUCTION

The rheological evaluation of viscoelastic polymer solutions is important in characterizing two-phase flow, aerodynamic breakup, dynamic contact angle and spreading behavior, and adhesive transfer of solutions between surfaces. Reactor product gels and other rheologically complex structures that have formed upon storage can be important to hazardous waste destruction (demilitarization) and require careful and controlled measurement by well-documented procedures. Documented procedures are also required for various engineering test plans. In addition, the process of laboratory certification for ISO Guide 25 requires thorough methodology documentation.

The preparation and measurement of polymer solution properties is an important aspect of several investigations and rather than report these methods separately, these techniques are gathered herein.

The preparation and sample history of polymer solutions can often influence the scientific and technological behavior of these complex systems because of the interplay of kinetic and thermodynamic effects. This is especially true in the case of complex gels, megadalton polymers [molecular weights (MW) of over 1 million], and theta solutions. Theta solution refers to polymer coils minimally expanded beyond the configuration maintaining intra-coil polymer contacts. The polymer might be considered marginally soluble for the specified solvent and temperature conditions.

The scope of the procedures described includes:

- Purification, grinding, and drying of polymer
- Solution preparation
- Sample preparation for Carbon-13 Nuclear Magnetic Resonance (NMR) analysis
- Solubility determinations
- Limiting viscosity number (LVN) measurements
- Rheological evaluation

In several instances, it was appropriate to include additional topics such as aspects of calibration, temperature control, and data treatment.

2. POLYMER SOLUTION PREPARATION AND SOLUBILITY DETERMINATION

2.1 Equipment and Procedures.

Solubility procedures have been documented for related studies,¹⁻⁶ and ASTM Method D3132-72 guidelines were incorporated.⁷

There is a need to prepare reproducible solutions, either as samples for evaluation or as reference/control standard solutions for comparison with unknown demilitarization reactor gel solutions. The instrumentation and equipment employed for polymer solution preparation, model identification, and manufacturer's address are listed in the appendix. The general procedures for preparing a polymer solution are detailed below.

Polymer solids of large particle size (>2 mm) were ground to fine particles (<1 mm) with a mortar and pestle or ball-mill and roller. In general, all custom synthesized polymers and most hygroscopic commercial polymers were dried in a Fisher (Model 48) vacuum oven at 20-25 in. Hg and 40 to 65 °C for at least 5 hr and up to several days. Liquid was added to a tared glass, polyethylene, fluorinated ethylene-propylene, or tetra-fluoroethylene bottle containing the appropriate amount of polymer sample. Total sample size ranged from about 2 to 10 g. Weighings were performed with sufficient accuracy and precision to report concentrations to at least two significant figures. The concentrations prepared ranged from about 1 to 10 g/dL depending on estimated polymer MW.

The techniques of adding polymer to liquid or liquid to polymer were developed to avoid agglomeration of powder particles and the consequent formation of large, slowly dissolving, polymer clumps. Keeping the sample under constant motion during addition and until installed in a shaker/mixer often maintained the polymer particles in a dispersed or non-aggregated state.

Sample positioning and mixing motions were selected so that all container surfaces were wetted and there was no residual dry or agglomerated polymer in containers or in cap screw threads. To avoid mechanical degradation of the polymer, no high shear mixing techniques were employed (e.g., rotary blade stirrers or sonic baths). Tumbling, rolling, two or three-dimensional shaking, and slow magnetic stir-bar mixing motions were employed.

The bottles were packed in one or more cushioned containers and mounted on one of the shakers or mixers. The shaker was adjusted to provide mixing of 60 to 160 cycles/min. Solvent systems, consisting of low toxicity organics, were mixed with polymers using a horizontal rolling motion at 100-180 cycles/min. These samples were packed (with the bottle sides horizontal) into a cylindrical container that was mounted between two rollers. Magnetic stir-bar rotation rate ranged from 30 to 60 rpm. Mixing was usually continuous until a solubility determination was completed.

Polymer solutions (previously determined to be thermodynamically stable at ambient temperature) could be prepared at slightly higher temperatures to accelerate the dissolution process. Higher temperature mixing could not be employed on initial solubility determinations because the polymer and liquid might not form a stable solution at ambient temperatures. However, these solutions might require weeks to coacervate and thus produce misleading rheological measurements during the extremely slow polymer precipitation process.

Modified procedures were used to prepare relatively high concentration, viscous polymer solutions for composition analysis by Carbon-13 NMR. Sufficient polymer to form a 6-10 wt % solution was weighed into a tared NMR tube (10 mm and 5 mm diameter tubes). The solid polymer was coated onto the NMR tube walls by rotating the horizontal tube. Addition of the solvent to the tilted NMR tube minimized polymer clumping and formation of a poorly mixed, swollen solid at the bottom of the tube. Deuterated solvents were used when possible. However, non-deuterated solvents were used if their presence did not interfere with the expected NMR spectrum of the polymer being analyzed. Conventional mixing techniques were applied for 3 to 7 days to enhance mixing within the tube. However, viscous solution motion was restricted within the tube.

2.2 Solubility Observations.

Polymer liquid samples were visually examined for dissolution. The appearance, the formation of gel particles, polymer swelling, the presence of ligaments or filaments, and other features were recorded at various intervals. Polymer-liquid samples of questionable or borderline solubility were drawn into and expelled from a syringe needle, and probed with a spatula to detect gel structures of similar refractive index to that of the polymer solution. Optically transparent structures were occasionally detected in this manner. A light source was projected into the sample to aid in detecting suspensions or inhomogeneous solutions. Polymer solutions were allowed to stand without mixing from several hours to several days before measurements were performed with the rheometer or other instruments. Observations for precipitation or other changes in appearance were made before measurements. The observation and recording of solubility results for data base capture has been standardized in our laboratory.⁸

3. DILUTE SOLUTION MEASUREMENTS OF LIMITING VISCOSITY NUMBER

Procedure.

Limiting viscosity number (LVN) measurement values are infinite dilution viscosity parameter extrapolations of polymer concentration. The LVN or intrinsic viscosity measurements were performed as specified in ASTM methods⁹ ANSI/ASTM D 2857-70 (Reapproved). Single point estimates of LVN were also employed.

Solution preparation was effected by weighing the sample in a container with foil-lined screw cap closure. Solvent was added by pipette and nitrogen layered gently on top before closure. They were stirred gently at room temperature for a minimum of three days on a magnetic stirrer. With each transfer of solution or solvent to the viscometer, there was a blanket of nitrogen added. Drying tubes containing calcium carbonate were placed atop the open side of the viscometers. Most experimentation was performed with a size 150 Cannon-Ubbelohde Dilution viscometer (Cannon Instruments, State College, PA). Approximate constant is 0.035 centistokes/sec, and the range is 7-35 centistokes.

The LVN values were obtained as the intercept from extrapolation of certain polymer solution viscosity terms to infinite dilution. The LVN is a function of polymer MW and polymer-liquid interaction. This interaction term is labeled the coil expansion coefficient "a." If the polymer composition and liquid are held constant, the LVN-MW relationship can be employed to empirically estimate polymer MW. If the polymer composition and polymer MW are held constant, the solvent effect on coil expansion can be measured. The third possibility of holding the solvent and polymer MW constant and employing LVN measurements to characterize the polymer composition effect is also possible. However, this is unrealistic because of the difficulty in obtaining a set of different polymer compositions having a constant MW. The heterogeneity of polymer MW and variability of MW distributions (MWD) does not allow one to hold this variable constant. In certain cases, however, measuring polymer MW by size exclusion chromatography (SEC) may allow factoring or normalization of MWD effects in a set of polymer compositions such that constant polymer MW, constant solvent composition investigation might lead to useful polymer composition effect relationships based on LVN measurements.

4. RHEOLOGICAL MEASUREMENT PROCEDURES

4.1 Instrumentation.

The Model RFR 7800 Rheometer (Rheometrics, Incorporated, Piscataway, NJ) was employed for steady shear measurement of first normal stress difference, apparent viscosity measurements, and oscillatory shear measurement of dynamic viscosity and moduli.

Additional rheological instrumentation was employed for special measurements. A vibrating oscillatory viscometer (VOV) was employed for high temperature measurements, especially when hazardous solvent systems were being investigated. In addition, comparative measurements were often obtained on polymer solutions measured with a glass capillary viscometer. The VOV imparts a high but known constant shear rate of 4053/sec. The glass capillary imparts a lower shear that varies but can be calculated from capillary dimensions and measurement time. In some cases, preliminary measurements were

performed with an LVT Model Wells-Brookfield Micro Viscometer (Wells-Brookfield, Middleboro, MA) or Cannon-Fenske Routine Glass Capillary Viscometers (Cannon Instrument Company, State College, PA).

4.2 Instrumental Conditions.

The rheometer experimental conditions are listed in Table 1. The value or range of values is noted in the first data column. Conditions applicable to all modes of stress are listed under "General" and those conditions applicable to a specific stress mode are listed separately. Experimental conditions that must be adapted to each sample are noted with the data.

The standard configuration for cone and plate measurement was rarely employed for hazardous polymer solutions. The conventional bottom plate was replaced by the cup fixture from the bob-and-cup fixture geometry. The cup provided containment of the hazardous polymer solution when the experiment was automatically ended by the sample spinning out of the gap at higher shear rates.

4.3 Rheometer Procedures.

The procedures employed in measuring the viscoelastic properties of polymer solutions (using the Rheometrics Model RFR 7800) can be found in the "Rheometrics Fluids Rheometer Operations Manual" (Rheometrics, Incorporated, Piscataway, NJ). The specific procedures not covered in the general manual are documented below.

(1) The test fixtures were mounted and the cone-to-plate or cone-to-cup gap was calibrated to 0 μm .

(2) A high intensity laboratory light beam was directed at the viscoelastic solution during all transfers to detect ligament and filament flow outside of the rheometer cup or sample containers.

(3) The polymer solution was introduced onto the center of the bottom plate by applying minimal pressure to a large bore (13-gauge) needle and polyethylene syringe. The sample volume injected was slightly higher than the calculated geometric volume under the cone (see Table 1).

(4) The sample was allowed to spread and de-bubble for several minutes, while being observed through a hinged mirror.

(5) The fixture was lowered onto the sample until initial contact was obtained and the solution was then allowed to relax until the Normal force transducer stabilized.

(6) The cone was further lowered to adjust the gap to 50 μm .

Table 1. Rheometer Experimental Condition for Measuring Viscoelastic Properties of Semi-Dilute Polymer Solutions

STRESS MODE	VALUE	REMARKS
GENERAL: ALL MODES		
Temperature mean, °C	23 to 27	Ambient
Temperature stability, °C	.2	±1
Gap, micrometers	50	
Fixture diameter, mm	50	
Cone angle, radians	0.0198	SN: 02; Nominal 0.02
Sample size, mL	0.66	±0.1; 1.13 mL, to 61 mm cup wall
Cone angle, radians	0.02	SN 13502; Nominal 0.02
Sample size, mL	0.66	±0.1; 1.13 mL, to 61 mm cup wall
Cone angle, radians	0.041	SN 708-00488/580; Nominal 0.04
Sample size, mL	1.35	±0.1; 1.13 mL, to 61 mm cup wall
Fixture diameter, mm:	25	
Cone angle, radians	0.040	SN 708-00487/579; Nominal 0.04
Sample size, mL	0.16	±0.1; 1.38 mL, to 61 mm cup wall
Cone angle, radians	0.099	SN 708-00486/581; Nominal 0.1
Sample size, mL	0.41	±0.1; 3.48 mL, to 61 mm cup wall
Rate range, points per (decade) torque range	Varied each experiment	Ranged from 6-10 points per decade
STEADY SHEAR MODE		
Direction	Both	Clockwise & counter-clockwise
Time to equilibrate, each direction; seconds	12	
Time to measure, each direction; seconds	12	
DYNAMIC MODE		
Correlate delay	Automatic 3 sec	
Frequency range, radians per second at strain %	1-100 at 20%	
THIXOTROPIC LOOP MODE		
Accelerate & decelerate time; seconds	30, 1-100/sec	Each direction, Zone 1
Points per decade	16	Each direction, Zone 2

(7) The viscoelastic solutions were then allowed to relax until a stable Normal Force transducer output was attained. Normal Force was then re-zeroed.

(8) Commands were programmed into the controller to apply the desired stress, to record the appropriate torque and/or normal force measurements, to compute the relevant rheological properties, and to print and/or plot the raw data. (Some of these parameters were set before loading the sample.) The experiment was started.

The rheological experiment ended in one of two ways. First and most frequently, the normal force or torque transducers were over-driven beyond their full-scale limits and a protective electronic circuit automatically terminated the experiment. Second, the polymer solution spun out of the gap at high rotational speeds, causing a sudden drop in the torque and normal force transducer output, and the operator then ended the experiment.

5. RHEOMETER CALIBRATION

5.1 Calibration of Torque and Normal Forces.

This calibration procedure is necessary to ensure the accuracy and precision of data acquired with this instrument. In this procedure, the torque force is completely calibrated at two FULL-SCALE settings and then the normal force is calibrated at two FULL-SCALE settings.

A digital multimeter was used to monitor output voltages and to verify the analog and digital displays on the front panel of the signal conditioner. All figures and sections referenced below are from the RFR 7800 manual.¹⁰

(1) Verify that dry air is being supplied to the rheometer air bearing by checking that the air gauges beside the rheometer cabinet register $>3.2 \text{ kg/cm}^2$ ($>45 \text{ psi}$), yielding a flow rate of 28 SLM (1 SCFM).¹⁰

(2) Attach the calibration fixtures and the air pulley to the rheometer transducer shaft as shown in Figure 6-3.¹⁰

(3) Turn on the main POWER [14] and the MOTOR [13] (Figure 3-1).¹⁰

5.2 Torque Force Calibration, 10 g-cm Full Scale.

(1) Connect a digital multimeter to the coaxial BNC Torque (T) output in the rear of the signal conditioner (Upper T in Table 3-4).¹⁰ Set the multimeter to a full-scale voltage of at least 5.0 V.

- (2) Set the STRAIN SERVO control [14] to DYNAMIC (Figure 3.2).¹⁰
- (3) Set the MODE control [5] to RATE SWEEP, the TEMPERATURE setting [4] to +700 °C, the RATE setting [6] to 0.9 rad/sec and the STRAIN percent to 20 [8] (Figure 3-3).¹⁰
- (4) Set the TRANSDUCER FULL-SCALE control [4] on the front panel of the signal conditioner to 10 g-cm (Figure 3.2).¹⁰
- (5) Set the analog meters for the TORQUE and NORMAL forces to zero by adjusting their FINE controls [2], (Figure 3.2).¹⁰ Check the accuracy of the TORQUE force by observing the multimeter that should read 0.00 ± 0.01 V. Adjust the TORQUE FINE control as necessary to bring the TORQUE force within this range.
- (6) Apply air to the air pulley by rotating the air control on the left side of the rheometer in a counter-clockwise direction (see Figure 3-1).¹⁰ Test airflow to the pulley bearings so the pulley will begin to rotate and increase in speed with the slightest push. When its rotation has been stopped, the pulley must remain stationary.
- (7) Press the START and the HOLD buttons. Allow at least one reading to be taken by waiting for the MEASURE IN PROCESS (MIP) light to come on and then go out. Monitor the digital TORQUE display and the multimeter and both should be <0.01 . Adjust the TORQUE FINE control as necessary.
- (8) Obtain a length of thread that extends from the torque calibration arm over the pulley and form a loop at each end. Slip one end of the line in the notch, at the end of the torque calibration arm, and extend the line full length over the pulley, being careful to apply a minimal, though preferentially zero, force to the arm. If too large a force is accidentally applied, the INPUT OVERLOAD light will come on. The instrument is then reset by pressing the RESET button and then repeat procedure from step 6 above.
- (9) Apply a 2-g weight to the end of the line as shown in Figure 6-3 and monitor the multimeter display, which should read (-4.000 ± 0.080) V, $(-3.920$ to $-4.080)$. Adjust potentiometer R10 on the TORQUE TRANSDUCER board in the signal conditioner cabinet as necessary (see Figure 6-2).¹⁰ When the multimeter reading is within specifications, wait for the MIP light to come on and go out once. The digital TORQUE display should read (-4.000 ± 0.080) . Remove the weight and thread and press the RESET button.

5.3 Torque Force Calibration, 100 g-cm Full Scale.

- (1) Set the TRANSDUCER FULL-SCALE control on the front panel of the signal conditioner to 100 g-cm.

(2) Repeat Steps 4, 6, and 7 of Section 5.2 above.

(3) Apply a 20-g weight to the end of the line as shown in Figure 6-3 and monitor the multimeter display, that should read (-4.000 ± 0.080) V, $(-3.920$ to $-4.080)$.

(4) Adjust potentiometer R16 at the far right on the TORQUE TRANSDUCER board in the signal conditioner cabinet as necessary (see Figure 6-2).¹⁰ Clockwise rotation increases the calibration value. When the multimeter reading is within specifications, wait for the MIP light to come on and go out once. The digital TORQUE display should read (-4.000 ± 0.080) .

(5) Remove the weight and thread and press the RESET button.

5.4 Normal Force Calibration, 10 g-cm Full Scale.

(1) Connect a digital multimeter to the coaxial Normal (Z) output in the rear of the signal conditioner. Set the multimeter to a full-scale voltage of at least 0.50 V.

(2) Set the STRAIN SERVO control to STEADY CW, the TEMPERATURE setting to $+25^{\circ}\text{C}$ and RATE setting to 1/sec. The MODE control remains at the RATE SWEEP setting.

(3) Set the TRANSDUCER FULL-SCALE control on the front panel of the signal conditioner to 10 g-cm.

(4) Set the analog meters for the TORQUE and NORMAL forces to zero by adjusting their FINE controls. Check the accuracy of the NORMAL force by observing the multimeter, which should read <0.001 V. Adjust the NORMAL FINE control as necessary.

(5) Turn on the Printer, press the SWEEP PARAMETERS button and correct/verify the following as necessary - last rate [1.000E+03], points per decade [10], readings per rate [1] and auto sweep [N].

(6) Press the START button and wait about 5-10 sec for the motor to come on.

(7) Press the READ FOR AVERAGE (RFA) button and wait for the MIP light to come on.

(8) About 3-5 sec after the MIP light comes on, press the RFA button so that it goes out.

(9) After the MIP light goes out, monitor the multimeter display, which should read <0.001 V. Monitor the digital NORMAL display, which should be <0.01 . Adjust the NORMAL FINE control as necessary.

(10) Place two 2-g weights (or sets of other weights adding to 4 g) on the fixture evenly spaced around the cone as shown in Figure 6-4¹⁰ and monitor the multimeter display, which should read (0.4000 ± 0.0080) V, (0.3920 to 0.4080). Adjust potentiometer R10 on the NORMAL TRANSDUCER board in the signal conditioner cabinet as necessary (see Figure 6-2).¹⁰

(11) When the multimeter reading is within specifications, repeat Steps 7 and 8 above.

(12) After the MIP light goes out, monitor the digital NORMAL display, which should read (0.4000 ± 0.0080) , (0.3920 to 0.4080). Remove the weights and press the RESET button.

5.5 Normal Force Calibration, 100 g-cm Full Scale.

(1) Set the multimeter full-scale voltage to at least 5.0 V or autorange.

(2) Set the TRANSDUCER FULL-SCALE control on the front panel of the signal conditioner to 100 g-cm.

(3) Set the analog meters for the TORQUE and NORMAL forces to zero by adjusting their FINE controls. Check the accuracy of the NORMAL force by observing the multimeter, which should read <0.01 V. Adjust the NORMAL FINE control as necessary.

(4) Repeat Steps 6, 7, and 8 of Section 5.4 above.

(5) After the MIP light goes out, monitor the multimeter and the digital NORMAL displays and both should be <0.01 . Adjust the NORMAL FINE control as necessary.

(6) Place two 20-g weights on the fixture as shown in Figure 6-4 and monitor the multimeter display, which should read (4.000 ± 0.080) V, (3.920 to 4.080). Adjust potentiometer R16 on the NORMAL TRANSDUCER board in the signal conditioner cabinet as necessary (see Figure 6-2).¹⁰

(7) When the multimeter reading is within specifications, repeat Steps 7 and 8 of Section 5.4 above.

(8) After the MIP light goes out, monitor the digital NORMAL display, which should read (4.000 ± 0.080) , (3.920 to 4.080). Remove the weights and press the RESET button.

(9) Turn off the MOTOR and remove the calibration fixtures and air pulley.

6. RHEOLOGICAL STANDARD FLUIDS

In addition to the direct calibration employing reference weights, calibration was performed by measurement of two classes of reference fluids. Newtonian viscometric fluids do not vary in viscosity as a function of shear rate. These fluids were employed to check and calibrate the torque transducer.

Table 2 documents examples of three types of Newtonian fluids used for evaluations of torque measurement performance. The second column contains a Cannon Certified Viscosity Standard with viscosity values at several temperatures. The viscosity-temperature values are plotted, and the rheometer measurement temperature is then interpolated to the viscosity at intermediate temperatures, usually between 20 and 25 °C. The next two columns contain sources of viscosity standards at one temperature. The first row identifies the standards name, and the second row provides an example of one of the viscosity series used. Other series fluids were employed to cover higher and lower viscosity values. The source address is provided in the third row. The remaining rows document the viscosity and temperature values for the examples.

Replacement standards in the same series have slightly different values. Standards between 5000 and 50 centipoise at 25 °C were employed most frequently. The 50-centipoise standards were only needed to check the performance at high shear rate, high torque, and the resultant low, shear-thinned, apparent viscosity values. Note that these viscometric standards did not shear thin to a standard viscosity but provided a constant Newtonian viscosity at the lower shear-thinned viscosities.

Rheological reference materials have been available for certifying the performance of shear-rate scanning rheometers. Examples of two rheological reference materials employed are documented in Table 3. The first column contains various descriptive parameters for the reference materials. The second and third columns contain the values for Standard Reference Material (SRM) 1490 and Research Material (RM) 40. The SRM provides certified values of viscosity and first normal stress difference (FNSD), while the RM category documents values obtained from a cooperative round robin measurement program. The second row lists the properties of the fluids that are standardized. The third row lists the National Institute for Standard Technology (NIST) source and address. The 'Composition' row documents the polymer and solvent systems used. The lack of documented concentration for SRM 1490 indicates that the concentration was to be adjusted to account for lot to lot variations in molecular weight in poly(isobutylene). The RM 40 co-solvent was later found to be somewhat toxic and required careful handling and disposal.

Table 2. Newtonian Viscometric Calibration Fluid Examples

Name	Certified Viscosity Standard	Brookfield Viscosity Standard	Viscosity Standard Kit
Series	S2000	Fluid 1000	Poly(dimethyl sil oxane) Component D
Source	Cannon Instruments PO Box 16 State College, PA 16801	Brookfield Engineering Lab. Straughton, MA 02072	Polysciences Inc. Warrington, PA 18976
Viscosity @ 20 °C	7908 centipoise		
Viscosity @ 25 °C	5009 centipoise	945 centipoise	930 centipoise
Viscosity @ 37.8 °C	1750 centipoise		
Viscosity @ 40 °C	1481 centipoise		
Viscosity @ 100 °C	59.3 centipoise		

Table 3. Rheological Reference Material Examples for Apparent Viscosity and First Normal Stress Difference (FNSD)

Name	Standard Reference Material 1490	Research Material 40 Lot 781130 (discontinued)
Property	Viscosity, First Normal Stress Difference	Nonlinear Flow Behavior: Viscosity and First Normal Stress Difference
Source	National Institute of Standards and Technology; BLDG. 202, Room 204; Gaithersburg, MD 20899 phone (301) 975-6776; fax (301) 948-3730, internet: http://www.nist.gov/srd/material.htm	
Composition	Polyisobutylene in Cetane	7.14 Wt/Wt % Polystyrene in 63.9% Tricresyl phosphate and 36.1% Aroclor-5432 Chlorinated biphenyl
Accuracy Viscosity	± 1%	
Precision FNSD	± 5% for extreme values	
Temperature	Zero Shear Viscosity; Density	Zero Shear Viscosity; Density
20 °C	530 poise; 0.7819 g/mL	1286 poise; 1.214 g/mL
25 °C	452 poise; 0.7802 g/mL	677 poise; 1.210 g/mL
30 °C	388 poise; 0.7784 g/mL	375 poise; 1.206 g/mL
35 °C	Not determined	222 poise; 1.202 g/mL
Temperature Coefficient	0.32% Viscosity Per 0.1 °C	1.5% Viscosity Per 0.1 °C 3% FNSD Per 0.1 °C

The accuracy values provided for SRM 1490 viscosity is $\pm 1\%$ at each shear rate and were based on Newtonian solutions certified to $\pm 0.5\%$. The FNSD has a specification for precision of $\pm 5\%$ for the range of extreme values. The next set of rows lists the temperature and resultant viscosity and density of the standard solutions. The densities are required to convert the dynamic viscosity values in poise to kinematic viscosity values in centistokes. The last row lists the temperature coefficient of viscosity and FNSD. The SRM 1490 has a low temperature coefficient of viscosity of $0.32\%/0.1\text{ }^{\circ}\text{C}$, while the RM 40 has a temperature coefficient of about $5\times$ this value, at $1.5\%/0.1\text{ }^{\circ}\text{C}$. (These standard solutions are no longer available from NIST. NIST has not yet made replacements available. Therefore, most investigators, including those in our laboratory, are using the archived samples and noting that they are past their expiration dates.)

The NIST rheological reference materials are unique. The rheological reference materials provided certified or documented viscoelastic values as a function of shear-rate. The values of apparent viscosity and FNSD are documented in Table 4. The first column lists the applied shear rate. The second and third columns list the resultant apparent viscosity and FNSD with their respective precision and accuracy values. The first set of rows contain the values for SRM 1490, and the second set of rows contain the values for RM 40. In general, the solutions of interest to our research were usually slightly lower in low shear viscosity than these standards.

Measurements of SRM 1490 were performed periodically, and examples of the experimental data sets are provided in Tables 5-7. Examples of the early baseline performance data sets are shown in Table 5. A comparison between different cone diameters and angles is shown for a fixture changeover in Table 6. A baseline on a different SRM 1490 lot is provided in Table 7.

In Tables 5-7, the first column lists the parameters describing the performance calibration experiment, and the remaining columns contain the experimental conditions and data sets. The first two rows contain the angle of the cone used and the diameter. The temperature range of the experiment is listed in rows three and four. The experimental identification is documented in the next row. The following rows contain the shear rate followed by the FNSD (in dynes/cm²) for each experiment. These values were monitored for comparison with the certified values for the SRM 1490 (see Table 4).

The figure shows an example of a plot for a calibration performance experiment. The x-axis lists the shear rate scan, and the y-axis contains the first normal stress difference. The experimental conditions are documented in Table 7, Experiment 165f.

7. CONCLUSION

The experimental procedures and calibration techniques developed for rheological research provided reliable, standardized methodology for investigation of the viscoelastic behavior of polymer solutions.

Table 4. Apparent Viscosity and First Normal Stress Difference (FNSD) Calibration Values as a Function of Shear Rate at 25 °C for National Institute of Standard Technology (NIST) Rheological Materials

Shear Rate, 1/sec	Viscosity, poise ($\pm 1\%$ accuracy)	FNSD, Newton/m ² ($\pm 5\%$ precision)
Standard Reference Material 1490:		
0.0177-0.07	452	
0.12	447	
0.56	408	13 ($\pm 10\%$)
1.11	356	33.5
2.22	308	77
4.45	241	160
8.80	179	310
17.7	125.5	540
35.5	83	910
70	53.5	1450
140	>32.5	
280	~19.7	
NIST Research Material 40:		
0.44-0.70	677	
1.4	677	27
2.8	643	98
5.5	578	290
11	491	770
22	382	1720

Table 5. Rheological Measurements of Shear Rate Versus First Normal Stress Difference (FNSD) for Standard Reference Material Viscoelastic Nonlinear Flow Behavior

Cone angle	.0198	.0198	.0198	.0198	.0198
Cone diameter, mm	50	50	50	50	50
Temperature lower	25.3	25.2	25.4	25.5	25.3
Temperature upper	25.5	25.4	25.5	25.5	25.5
Shear Rate	13a	13c	130a	130b	148a
1.000	134.2	134.0	30.69	81.39	85.93
1.259			160.5	251.6	214.0
1.585	268.1	261.1	232.4	350.1	325.8
1.995			386.7	466.0	509.8
2.512	451.3	447.8	449.0	608.2	835.8
3.162			660.5	759.1	885.3
3.981	778.9	776.9	784.2	982.5	1356.
5.012			1089.	1236.	1419.
6.309	1283.	1296.	1343.	1563.	2120.
7.943			1769.	1909.	2275.
9.999	2130.	2079.	2196.	2383.	2975.
12.59			2764.	2934.	3422.
15.85	3250.	3208.	3377.	3542.	4123.
19.95			4148.	4302.	4936.
25.12	4830.	4762.	5014.	5213.	5730.
31.62			6045.	6206.	6732.

Table 6. Rheological Measurements of Shear Rate Versus First Normal Stress Difference (FNSD) for Standard Reference Material 1490 Lot 810608 as a Performance Calibration for Viscoelastic Nonlinear Flow Behavior

Cone angle	.0198	.0198	.0198	.0198	.0198	0.099	0.099
Cone diameter	50	50	50	50	50	25	25
Temperature lower	25.4	25.5	21.9	25.0	24.8	25.3	25.6
Temperature upper	25.6	25.7	22.3	25.2	25.0	26.2	26.7
Shear Rate	148b	148c	159b	159c	159d	163e	164a
1.000	82.06	47.87	55.11	73.49	109.9	244.8	200.7
1.259	195.8	153.0	205.6	145.5	259.2	337.0	266.6
1.585	325.2	227.9	348.9	302.7	320.5	447.3	373.2
1.995	530.6	516.9	537.3	365.9	534.5	597.2	533.7
2.512	640.2	497.8	696.1	587.9	644.3	792.5	726.6
3.162	773.9	812.9	968.6	724.7	890.2	1035.	980.3
3.981	786.5	813.0	1225.	1042.	1065.	1334.	1280.
5.012	1313.	1499.	1611.	1274.	1423.	1698.	1659.
6.309	1293.	1434.	2009.	1710.	1707.	2140.	2125.
7.943	2110.	2219.	2578.	2081.	2232.	2666.	2662.
9.999	2177.	2262.	3158.	2646.	2666.	3294.	3326.
12.59	2909.	3073.	3962.	3247.	3376.	4047.	4110.
15.85	3548.	3656.	4796.	3948.	4061.	4911.	5015.
19.95	4191.	4273.	5840.	4861.	4978.	5854.	6024.
25.12	5257.	5279.	6957.	5741.	5913.	6882.	7123.
31.62	6155.	6117.		6861.	7061.	7993.	8295.
39.80	7211.	7284.				9156.	9529.
50.11						10250.	10730.
63.08						11180.	11790.
79.42						12150.	12980.
99.98						13040.	13060.

Table 7. Rheological Measurements of Shear Rate Versus First Normal Stress Difference (FNSD) for Standard Reference Material 1490 Lot 580905 as a Performance Calibration for Viscoelastic Nonlinear Flow Behavior

Cone angle	.0198	.0198	0.041	0.041	0.040	0.040	0.099
Cone diameter	50	50	50	50	25	25	25
Temperature lower	24.8	24.8	24.9	24.9	24.9	24.9	24.8
Temperature upper	25.0	25.0	25.1	25.1	25.1	25.1	25.2
Experiment #	165a	165b	165c	165d	165e	165f	165g
Shear Rate 1/sec							
1.000	93.82	120.9	254.7	235.4	224.0	259.8	214.6
1.259	196.3	206.1	266.6	313.2	257.6	398.5	280.0
1.585	262.7	319.2	391.8	457.4	353.9	517.1	386.9
1.995	412.9	416.1	501.0	581.7	476.0	704.3	525.0
2.512	481.6	551.4	754.3	760.1	613.0	806.1	689.4
3.162	724.6	698.9	949.5	967.9	799.5	1067.	914.9
3.981	842.1	944.0	1288.	1211.	1060.	1279.	1195.
5.012	1192.	1191.	1595.	1521.	1336.	1611.	1528.
6.309	1402.	1527.	2006.	1892.	1647.	1996.	1926.
7.943	1897.	1888.	2450.	2351.	2070.	2393.	2438.
9.999	2220.	2371.	2994.	2892.	2538.	2953.	3012.
12.59	2866.	2901.	3633.	3523.	3153.	3548.	3723.
15.85	3460.	3503.	4393.	4261.	3831.	4311.	4545.
19.95	4221.	4242.	5211.	5081.	4493.	5114.	5498.
25.12	5042.	5037.	6192.	6057.	5440.	6005.	6579.
31.62			7303.		6513.	7143.	7722.
39.80					7717.	8426.	8936.
50.11					9122.	9819.	10250.
63.08					10750.	11470.	11690.
79.42					12750.	13310.	13160.
99.98					14970.	15330.	
125.9					17140.	17580.	
158.5					19630.	20120.	
199.5					22430.	22960.	
251.1					25590.	26160.	
316.2					29370.	29930.	
398.0					34130.	34620.	

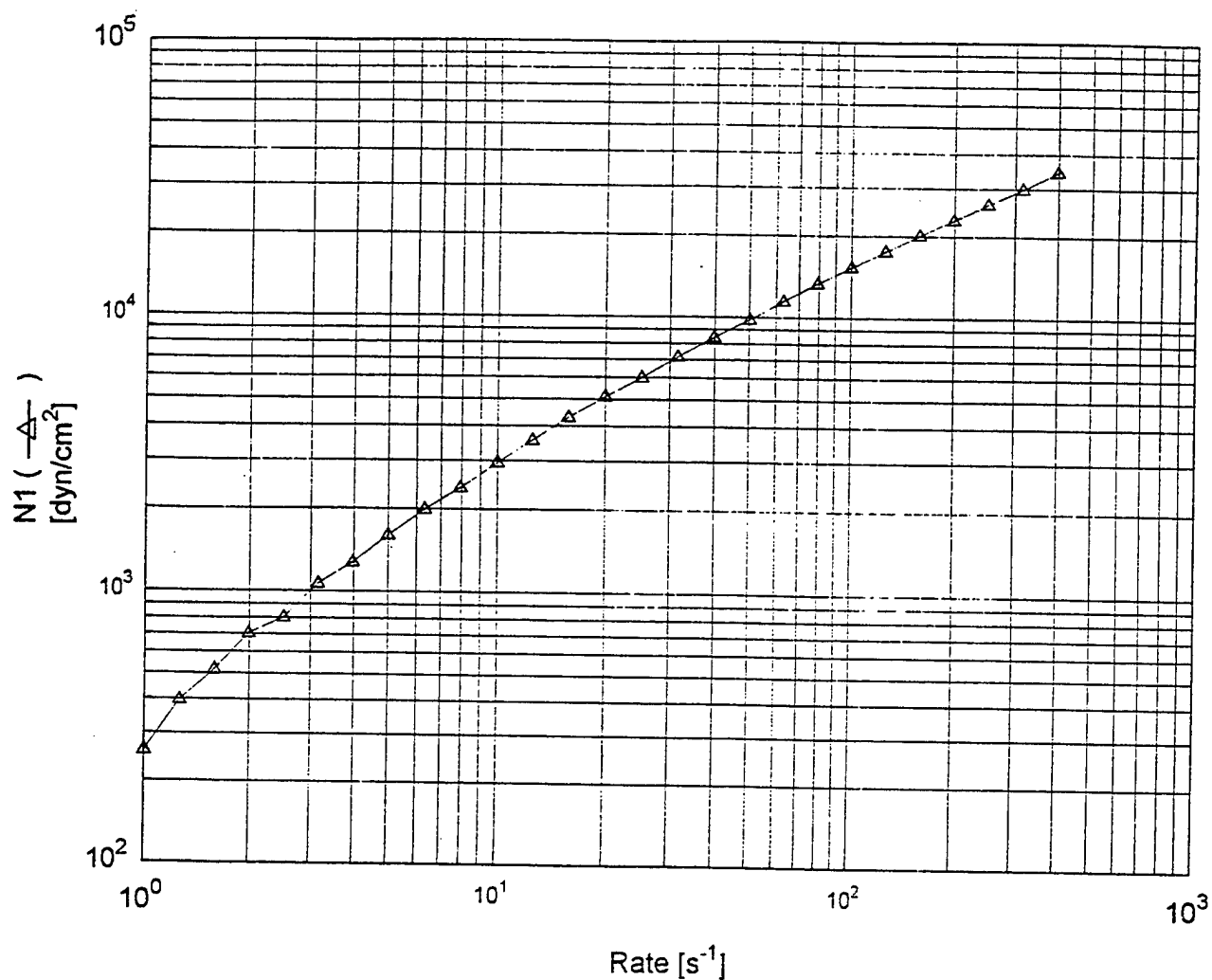


Figure. Rheological Plot of First Normal Stress Difference (FNSD) Versus Shear Rate for NIST Standard Reference Material 1490 at 24.9 to 25.1 °C (see Table 7, Experiment 165f).

LITERATURE CITED

1. Shuely, Wendel J.; and Ince, Brian S.; "Rheological Properties of High- Molecular Weight Poly[(methyl methacrylate)-co-ethyl-acrylate-co-butyl-acrylate] Solutions: Influence of Polymer-Solvent Interactions," In Polymers as Rheology Modifiers, ACS Symposium Series 462, Schulz, Donald N.; and Glass, J. Edward; Eds., American Chemical Society, Washington, DC, 1991.
2. Wang, J.; Pfeiffer, D. G.; Shuely, W. J.; and Chu, B.; "Rheological Properties and Association Behavior of Mixtures of Poly[isobutylmethacrylate-(tert-butylamino)ethyl methacrylate] and an Ionomer in Solution," Macromolecules Vol. 24, pp 4349-4355 (1991).
3. Shuely, W. J.; and Ince, B. S.; Rheological Measurement of Solvent Effects on Viscoelastic Properties in the Semidilute Regime, in the Proceedings of the International Polymer Processing Society Fourth Annual Meeting, American Institute of Physics, Melville, NY, May 1988.
4. Shuely, W. J.; and Ince, B. S.; "Influence of Polymer-Solvent Interactions on the Rheological Properties of Megadalton Poly (MMA/EA/BA) Solutions," ACS, Polym. Mater. Sci. Eng. Vol. 61, pp 161-165 (1989).
5. Hong, Seok H.; and Shuely, Wendel J.; "Influence of Trace Components on the Viscoelastic Properties of a Polymer Solution Extended Abstracts of Polymer Chemistry," American Chemical Society Polymer Preprints Vol. 33, p 282 (1992).
6. Chu, Benjamin; Wang, Jian; Pfeiffer, Dennis G.; and Shuely, Wendel J.; "Effects of an Ionomer Additive on the Rheological Properties of a Random Copolymer Poly(isobutylmethacrylate-(tert-butylamino) ethyl methacrylate)," Macromolecules Vol. 24(3), pp 809-811 (1991).
7. ASTM D3132 Standard Test Method for Solubility Range Of Resins And Polymers. Annual Book of ASTM Standards, Vol. 08.01 Plastics (1) C177-D 1600, American Society for Testing and Materials Headquarters, West Conshohocken, PA, 1992.
8. Shuely, Wendel J.; Polymer Solubility Experimentation: ASTM D3132 Test Report Database Documentation. Volume I, ERDEC-SP-041, U.S. Army Edgewood Research, Development and Engineering Center, Aberdeen Proving Ground, MD, April 1996.
9. ASTM D2857 Standard Test Method for Dilute Solution Viscosity of Polymers, Annual Book of ASTM Standards, Volume: Coatings, American Society for Testing and Materials Headquarters, West Conshohocken, PA, 1992.
10. Rheometrics Fluids Rheometer, Operations Manual, Version RFR-7800 3.0, Rheometrics, Incorporated, One Possumtown Road, Piscataway, NJ, 1983.

Blank

APPENDIX

INSTRUMENTATION AND EQUIPMENT EMPLOYED FOR POLYMER SOLUTION PREPARATION

RHEOMETERS AND VISCOMETERS:

Rheometric Fluids Rheometer, RFR 7800 Operations Manual, Rheometrics, Incorporated, One Possumtown Road, Piscataway, NJ 08854.

Vibrating Oscillatory Viscometer, Nametre Model Lab 396G81; Edison, NJ

LVT Model Wells-Brookfield Micro Viscometer, size 150, Wells-Brookfield Company, Middleboro, MA.

Cannon-Fenske Routine Glass Capillary Viscometer, size 150; Cannon Instrument Company, State College, PA.

MIXERS:

Roller, Serial No. CK-64125, U.S. Stoneware, Akron, OH

Turbula Shaker, Type T2C, Impandex, Incorporated, 203 Brookdale St., Maywood, NJ 07607

Fisher-Kendall Mixer, Model 12-811V2, Fisher Scientific Company, 711 Forbes Ave., Pittsburgh, PA 15219

Lab-Line Orbit Environ-Shaker, Model 3527, Lab-Line Instruments, Incorporated, Lab-Line Plaza, Melrose Park, IL 60160

Shaker Power Unit, Catalog 6000, Reciprocating, Variable Speed, used with Utility Box Carrier, Catalog 6040, Eberbach Corporation, PO Box 1024, Ann Arbor, MI 48106

BALANCES:

Balance, Model AT261 and H15, Mettler Instrument Corporation, PO Box 71, Hightstown, NJ 08520

Balance, Model PL 3000, Brinkmann Instruments Company, Cantiague Road, Westbury, NY 11590